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14. ABSTRACT The DURIP grant has been used to purchase two new infra-red laser systems that have been used to initiate combustion of energetic aerosol particles. One is a CO ₂ laser capable of delivering up to 1.5 J of pulsed power, while the other is an OPO laser pumped by an existing Nd:YAG laser to provide tunable radiation in the 2.7 to 3.3 μm range. These lasers have been used to help unravel the decomposition of base catalyzed nitromethane, CH ₃ NO ₂ . The first four steps in its decomposition have been confirmed by the first positive experimental identification of seven intermediates including CH ₂ NO ₂ ⁻ , R ₂ NH ₂ ⁺ , NO ₂ ⁻ , RNH ₃ ⁺ , and NH ₄ ⁺ . In addition, a controversial reaction step was confirmed by isotopic labeling studies. The mechanism for the base catalyzed nitromethane decomposition is now established. The study of aerosol particles has been advanced by the development of methods to create coated particles and to carry out depth profiling using variable power IR laser heating. The ability to create particles with heterogeneously mixed core and outer layer, coupled with the tunability of the OPO infra-red laser has made it possible to ignite a particle from either the core or from the outside. Finally, a method employing a "chemical thermometer" has been developed to monitor the temperature of a rapidly combusting particle. The thermometer is the dissociation of glycerol ions, which produces parent and two daughter ions whose intensities depend strongly on the ion vibrational energy.					
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Progress Report – September, 2001

Laser Initiated Decomposition in Aerosol Fuels: A method for probing the early stages of ignition and detonation

DURIP Grant F49620-00-1-0191

Tomas Baer and Roger E. Miller

Department of Chemistry

University of North Carolina

Chapel Hill, NC 27599-3290

Summary:

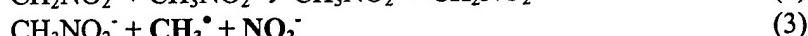
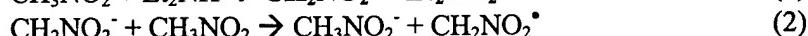
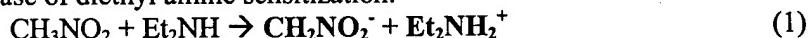
The DURIP grant has been used to purchase two new infra-red laser systems that have been used to initiate combustion of energetic aerosol particles. One is a CO₂ laser capable of delivering up to 1.5 J of pulsed power, while the other is an OPO laser pumped by an existing Nd:YAG laser to provide tunable radiation in the 2.7 to 3.3 μm range. These lasers have been used to help unravel the decomposition of base catalyzed nitromethane, CH₃NO₂. The first four steps in its decomposition have been confirmed by the first positive experimental identification of seven intermediates including CH₂NO₂⁻, R₂NH₂⁺, NO₂⁻, RNH₃⁺, and NH₄⁺. In addition, a controversial reaction step was confirmed by isotopic labeling studies. The mechanism for the base catalyzed nitromethane decomposition is now established. The study of aerosol particles has been advanced by the development of methods to create coated particles and to carry out depth profiling using variable power IR laser heating. The ability to create particles with heterogeneously mixed core and outer layer, coupled with the tunability of the OPO infra-red laser has made it possible to ignite a particle from either the core or from the outside. Finally, a method employing a “chemical thermometer” has been developed to monitor the temperature of a rapidly combusting particle. The thermometer is the dissociation of glycerol ions, which produces parent and two daughter ions whose intensities depend strongly on the ion vibrational energy.

A. The experimental Approach

Aerosol particles of known composition and a broad range of diameters from .3 to 5 μm can be created by a nebulizer. This method uses very small quantities of sample, an important consideration when generating particles with energetic materials. These particles are introduced through a 100 μm orifice into an aerodynamic lens system that focuses the particles onto a 2 mm nozzle. The rapidly accelerated particles then enter the vacuum chamber via two stages of differential pumping. The particle velocity, and thus the particle size, is determined by light scattering signals from two green diode laser beams that intersect the particle path and are spaced 10 cm apart. The IR CO₂ laser or the Nd:YAG pumped OPO laser that initiates the ignition of the particle is fired when the particle reaches the ionization region. A vacuum UV laser (10.48eV), generated by tripling the 355 nm output of the Nd:YAG laser, photoionizes the molecules and permits the identification by time of flight mass spectrometry.

B. The initial states of nitromethane Decomposition:

In a 1998 paper, Gruzdkov and Gupta (J. Phys. Chem. A 1998, 102, 2322) suggested that the amine sensitized decomposition of nitromethane involves steps (1) to (3) of the following mechanism, shown for the case of diethyl amine sensitization:



The first two steps in this mechanism are controversial because nothing is known about their thermochemistry in neat nitromethane liquid. Gruzdkov and Gupta suggested this mechanism on the basis of transient absorption experiments in which they detected a species with an absorption peak between 500 and 550 nm. They proposed that this must be due to a free radical and proposed CH_3NO_2^- as a likely candidate. This was the first and only experimental evidence for any species involved in this decomposition. We investigated this reaction by CO_2 laser decomposition of aerosol particles consisting of 1% diethyl amine in pure nitromethane. The intermediate products were detected by TOF mass spectrometry. Ion and neutral intermediates were readily distinguished by the fact that the former could be detected without the VUV laser probe pulse, while the latter required the VUV laser. This study provided positive identification of the seven species shown in bold in reactions (1) to (5). The most controversial step in this mechanism is reaction (2), because this reaction in the gas phase would be endothermic by 212 kJ/mol. However, our studies using deuterium labeled nitromethane provided strong support for this step. These results have been published in an article about to appear in the J.Phys.Chem.A.

C. Chemical Thermometers

While our method of laser ignition and product detection is a very powerful approach for detection of reaction intermediates, it suffers from the lack of information about the ignition conditions, in particular the temperature. We have thus developed a chemical thermometer that can provide some of this information. The method, based on the known decomposition of a probe molecular ion as a function of its internal energy, involves seeding a combustion mixture with a few percent of this molecule and detecting the dissociative photoionization products during the combustion process. The properties of this probe molecule should be the following: (a) it should not interfere with the combustion process, (b) it should be quite stable in its neutral form, (c) it should have an ionization energy close to the VUV laser energy of 10.4 eV, (d) it should have at least two dissociation products that vary in intensity with the ion internal energy. An ideal molecule for this process appears to be ethylene glycol.

The procedure for determining the temperature is illustrated in Figure 1. The solid lines show the parent and the two product ions as a function of the ion internal energy. The dotted line is the internal energy distribution, $P_E(E,T)$ at some temperature, T , of the neutral molecule before ionization. Ionization simply transposes this distribution to the ion manifold. By convoluting the internal energy distribution, $P_E(E,T)$ with the parent ion function, $P^+(E)$, with the following integral, we can calculate the parent ion peak height in the mass spectrum.

$$P^+(T) \propto \int_0^\infty P^+(E) P_E(E,T) dE \quad (6)$$

Similar integrals give the yield of production, $D1^+$ and $D2^+$. Thus, by comparing the measured signal intensities of parent and the two daughter ions with those predicted by the above integrals using various temperatures to calculate the $P_E(E,T)$ function, we can determine the temperature of the ethylene glycol molecule in the ignited particle. Because we measure three ion signals, we can determine whether the product internal energy distribution can be described by a temperature, or whether the system is a non-canonical one. These results are being written up as an article in the J.Phys.Chem. A.

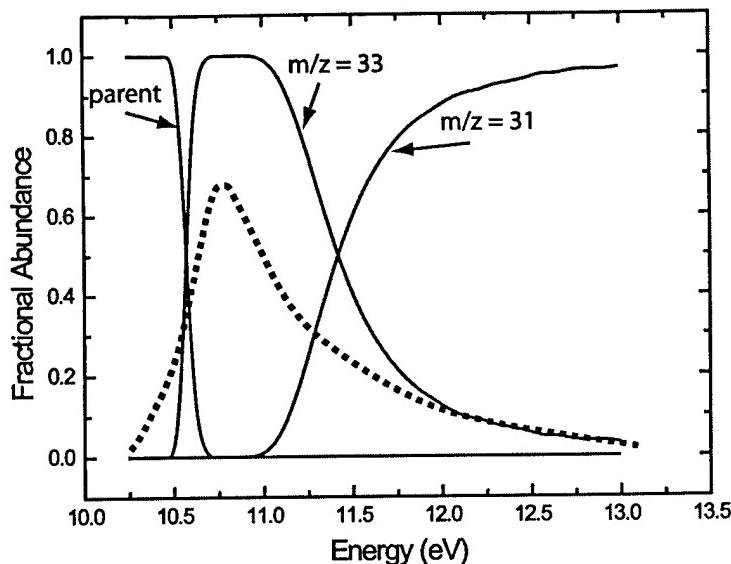


Figure 1. The breakdown diagram of ethylene glycol (determined in our photoelectron photoion coincidence experiment) in which the fractional abundance of parent, $P^+(E)$, and fragment ions are plotted as a function of the ion internal energy. The dashed line is a calculated glycerol thermal energy distribution at a given temperature from which the mass spectrum as a function of the temperature can be derived.

D. The production and analysis of coated particles

One of the goals of our research with energetic materials is to prepare samples that are heterogeneously or homogeneously mixed. In this fashion it may be possible to observe the difference between very rapid reactions and those that are limited by diffusion of one species into the other. An additional reason is the ability to coat an energetic sample with an outer layer that prevents the quick escape of reactive intermediates, thereby forcing them to react further in a high-density environment. This could be achieved by choosing an outer layer that does not absorb the igniting laser radiation so that only the inner core would be heated.

The key to preparing coated particles is the use of insoluble molecules. We have recently produced heterogeneously mixed particles and have developed the tools to analyze them. The samples involved are glycerol and oleic acid. Glycerol is a good low vapor pressure proxy for water, while oleic acid with its 18 unit long hydrocarbon chain is an oil. Thus the two are insoluble. The high surface tension and strong intermolecular attractions in glycerol favor its localization in the core of the aerosol particle. Thus, we can prepare them by passing glycerol particles through a tube containing oleic acid vapor. Alternatively, glycerol, oleic acid, and isopropanol can be pre-mixed (oleic acid and glycerol are mutually soluble in sufficient quantities of isopropanol) and the solution used to generate aerosol particles with a vibrating orifice aerosol generator (VOAG). Upon drying off the isopropanol, the glycerol and oleic acid phase separate, which results in the production of coated particles.

The morphology of the particles can be verified by the use of variable power IR lasers to partially vaporize the particles. At low powers, only the outer layer will evaporate and the mass spectrum will be rich in the oleic acid, while at higher powers the complete particle will be vaporized and the relative mass peak intensities of oleic acid and glycerol will reflect their proportion in the sample. Figure 2 shows an example of such an analysis for the case of glycerol coated with a 100 nm layer of oleic acid. A paper on this topic is being submitted to the J.Phys.Chem. A.

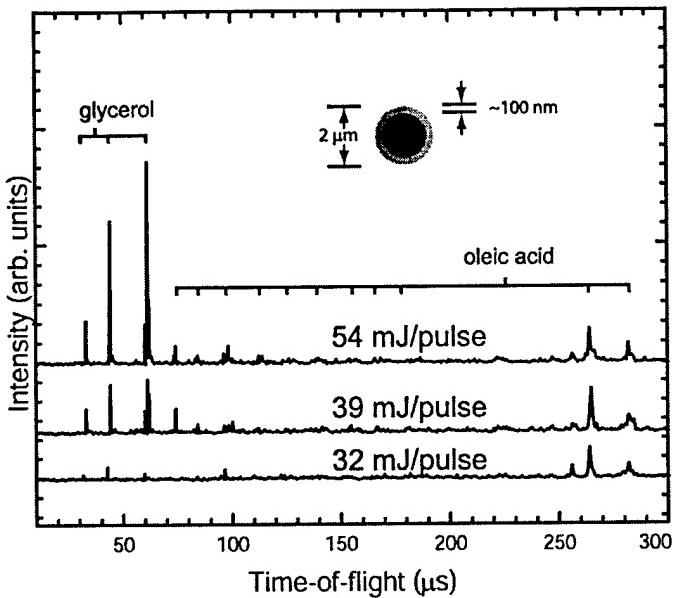


Figure 2. The mass spectra of glycerol particles coated with oleic acid as a function of the CO₂ laser power. Note the appearance peaks associated with the outer of oleic acid before the core ion peaks appear.

C. Selective excitation of the core or outer layer by tunable OPO generated IR radiation

One of the uses of the new OPO laser is the ability to tune the IR radiation so that certain molecules can be selectively excited. We have demonstrated this with glycerol particles coated with a layer only 60 nm thick of oleic acid. As shown in Figure 3, the absorption spectra of glycerol and oleic

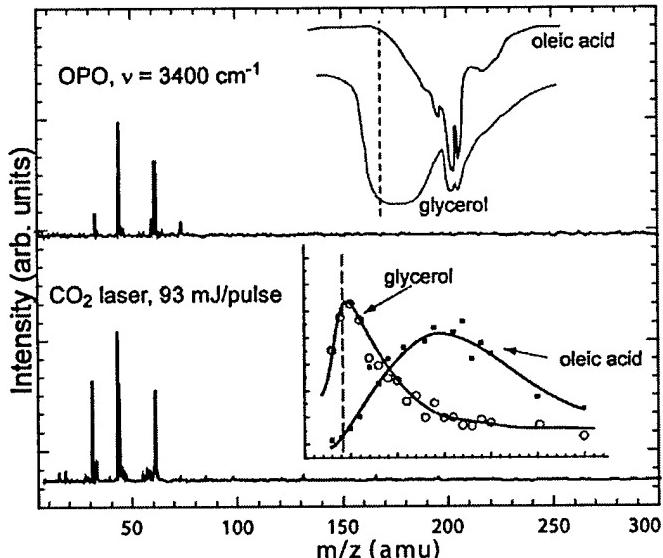


Figure 3: The mass spectra of coated aerosol particles vaporized by IR lasers and ionized by the VUV laser. In the top spectrum, the OPO laser is tuned to the OH stretch mode of glycerol so that only this molecule is observed in the mass spectrum, independent of the time of observation. On the other hand, under CO₂ laser irradiation, both glycerol (core) and the outer layer of oleic acid mass peaks are observed. However, they are separated in time. This observation is presently being interpreted.

acid are such that tuning the OPO laser to 3400 cm^{-1} excites only the OH vibrations in glycerol and does not excite the oleic acid modes. As a result, we see the mass spectra of only the glycerol core. On the other hand, with the CO₂ laser excitation, the glycerol mass signal is seen at early times, but signal due to oleic acid, which also absorbs the CO₂ radiation, is observed at later times.

Future Plans:

Having developed the tools to generate and analyze coated particles, we are now ready to embark on the next combustion study. We will generate particles with a core of alumina and an outer layer of TNT, or nitromethane in order to initiate the combustion from the inside. A second high priority project is the use of the chemical thermometer in the nitromethane and TNT reactions. A final project is the preparation of variable sized particles and the use of coated particles to determine the effect confinement on the combustion dynamics.

Papers published or submitted based on the equipment from the DURIP grant:

- E. Woods III, Y. Dessiaterik, E.R. Miller, and T. Baer, "Dynamics in the Early Stages of Decomposition In Liquid Nitromethane and Nitromethane-Diethylamine Mixtures" *J. Phys. Chem.* **105** 8273- 8280 (2001)
- C. Sykes, E.Woods III, G.D. Smith, R.E. Miller, and T. Baer, Single aerosol particle analysis with thermal vaporization detection and VUV laser ionization mass spectrometry" *Anal.Chem.* submitted (2001)
- E. Woods, III, G.D. Smith, T. Baer, and R.E. Miller, "Analysis of heterogeneously mixed aerosol particle morphology by IR laser vaporization, VUV laser ionization mass spectrometry" *J.Aerosol Sci.* to be submitted (2001)
- E. Woods, III, G.D. Smith, Y.Li, R.E. Miller, and T. Baer, "Internal temperature of IR laser vaporized aerosol particles determined by a "chemical thermometer""", *J.Phys.Chem.A* to be submitted (2001)
- G.D. Smith, C. Hauser, E.Woods III, T. Baer, and R.E. Miller "The heterogeneous reaction of ozone with oleic acid aerosol particles studied by flow tube and single particle laser TOF mass spectrometry", *J.Phys.Chem.A* to be submitted (2001)